Quantifying microbial methane oxidation efficiencies in two experimental landfill biocovers using stable isotopes

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ABSTRACT

Stable isotope analyses were performed on gas samples collected within two instrumented biocovers, with the goal of evaluating CH_4 oxidation efficiencies (f_0). In each of the biocovers, gas probes were installed at four locations and at several depths. One of the biocovers was fed with biogas directly from the waste mass, whereas the other was fed through a gas distribution system that allowed monitoring of biogas fluxes. While the f_0 values obtained at a depth of 0.1 m were low (between 0.0 and 25.2%) for profiles with poor aeration, they were high for profiles with better aeration, reaching 89.7%. Several interrelated factors affecting aeration seem to be influencing f_0, including the degree of water saturation, the magnitude of the biogas flux, and the temperature within the substrate. Low f_0 values do not mean necessarily that little CH_4 was oxidized. In fact, in certain cases where the CH_4 loading was high, the absolute amount of CH_4 oxidized was quite high and comparable to the rate of CH_4 oxidation for cases with low CH_4 loading and high f_0. For the experimental biocover for which the CH_4 loading was known, the oxidation efficiency obtained using stable isotopes (f_0 = 55.67% for samples taken inside flux chambers) was compared to the value obtained by mass balance (f_0 = 70.0%). Several factors can explain this discrepancy, including: the high sensitivity of f_0 to slight changes in the isotopic fractionation factor for bacterial oxidation, α_{ox}, uncertainties related to mass flow meter readings and to the static chamber method.

Keywords: *methane oxidation, biocovers, carbon stable isotopes, landfill.*

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1. INTRODUCTION

Methane (CH_4) is a greenhouse gas with an infrared activity 25 times that of CO_2 (IPCC 2007) and its atmospheric concentration is increasing at a rate of 0.6% per year (IPCC 2001). Landfills represent an important source of CH_4 emissions and, according to several sources (e.g. Bogner and Matthews 2003; De Visscher et al. 2004; Stern et al. 2007; Chanton et al. 2008), their contribution to the global CH_4 emissions may vary from 3 to 10%. Therefore, management practices that could help reduce emissions from landfills are of great importance in connection with the atmospheric CH_4 budget. Gas extraction systems, which are now widely adopted in the developed world, are considered the principal means of achieving such reductions. However, gas collection systems are not 100% efficient; indeed, it has been reported that even at sites with gas collection systems, significant amounts of biogas can still escape as fugitive emissions (e.g. Spokas et al. 2006; Börjesson et al. 2007).

According to the Working Group III of the Intergovernmental Panel on Climate Change, one promising management strategy to reduce emissions from landfills is the installation of a biocover as part of the final cover system (IPCC 2007; Table SPM 3). When a final cover is engineered to optimize the growth and activity of the methanotrophic bacteria, it becomes a passive methane oxidation biocover (PMOB). In PMOBs, CH_4 reduction is regulated by methanotrophic bacteria that develop in the aerobic zone near the surface. The microbial oxidation of methane for the abatement of landfill methane emissions is not only applicable as a complement to gas extraction, but is also suited to treat residual emissions during aftercare or low calorific emissions from wastes that have a low gas generation rate.

Methanotrophs in landfill covers or biofilters are capable of converting CH_4 to CO_2 and biomass in the presence of atmospheric O_2 (e.g. Boeckx et al. 1996; Humer and Lechner 1999; Boeckx and Van Cleemput 2000; Hilger and Humer 2003; Gebert and Gröngröft 2006; Stern et al. 2007). The process of microbial oxidation is influenced by several factors, including, among others, the temperature within the cover, the diffusivity of the cover material and the magnitude of biogas flux. The latter partly depends on the differential pressure between the waste mass and the atmosphere that also partly controls the availability of O_2, and the air-filled porosity, which also depends on the amount of water infiltration through the top cover.

Despite the promising future of biocovers, the reliability of methods to estimate CH_4 oxidation efficiency of biocovers in the field remains a problem. It is indeed difficult to estimate efficiencies without knowledge of the CH_4 fluxes reaching the base of a cover and leaving it, moreover when emissions may span over 7 orders of magnitude (Bogner et al. 1997), and important variations in the magnitude of emissions may be found within the same landfill (Czepiel et al. 1996; Scheutz et al. 2003). A technique that has been recently employed in several field studies

estimates CH_4 oxidation efficiency in landfill covers based on changes in the ratio of two stable carbon isotopes, namely ^{13}C and ^{12}C (Liptay et al. 1998; Chanton and Liptay 2000; De Visscher et al. 2004; Chanton et al. 2008). While ^{12}C is 99% abundant, ^{13}C responds for the remaining 1%.

This paper presents the results obtained from the stable isotope analysis performed on gas samples collected during the 2007 monitoring campaign of two PMOBs installed at the St-Nicéphore landfill, Quebec, Canada, a waste disposal facility covering approximately 65 hectares that receives mainly domestic waste. The goal was to estimate the biotic methane oxidation efficiencies of the two PMOBs. Gas samples were frequently taken at several locations and depths within the PMOBs. For clarity, the main design characteristics of the PMOBs and the instrumentation installed are described.

2. BACKGROUND

The carbon stable isotope composition is expressed as follows (e.g. Chanton et al. 1999):

$$\delta^{13}C(‰) = \left[\left(\frac{R_{sample}}{R_{standard}}\right) - 1\right] \times 1000 \quad (1)$$

where R_{sample} is the $^{13}C/^{12}C$ ratio of the sample and $R_{standard}$ is the $^{13}C/^{12}C$ ratio of the reference standard VPDB (Vienna Peedee Belemnite; $R_{standard}$ = 0.01124).

Studies using methanotrophic cultures have shown that the lighter isotope ^{12}C is oxidized more rapidly than the heavier isotope ^{13}C, (Chanton and Liptay 2000; De Visscher et al. 2004). As a result, changes in isotope composition occur when methane is oxidized, altering the isotope ratio. Indeed, $\delta^{13}C$ values of CH_4 produced in the deepest zone of the landfill profile are typically between - 50 and - 61‰, and the $\delta^{13}C$ values of emitted CH_4 are generally between -30 and -50‰ (Chanton et al. 1999). Knowledge of $\delta^{13}C$ values of the CH_4 produced and emitted allows calculating the fraction of methane that is oxidized when fugitive emissions of biogas migrate through the top cover (De Visscher et al. 2004). The percentage of CH_4 oxidized (or oxidation efficiency, f_0) is determined by the following equation (taken from Abichou et al. 2006a):

$$f_0 = 0.1 \times \frac{\delta_E - \delta_A}{\alpha_{ox} - \alpha_{trans}} \quad (2)$$

where δ_A is the $\delta^{13}C$ value of the anoxic zone; δ_E is the $\delta^{13}C$ value of emitted CH_4; α_{ox} is the isotopic fractionation factor for bacterial oxidation; and α_{trans} is the isotopic fractionation factor associated with gas transport.

The fractionation factor for microbial oxidation α_{ox} can be obtained empirically (Liptay et al. 1998; De Visscher et al. 2004). Previous studies pertaining to landfill emissions reported different values of α_{ox}, some of which are summarized in Table 1 (with the associated temperatures prevailing when the samples were taken). The variation of soil temperature modifies the fractionation factor value and, therefore, the calculated methane oxidation efficiency. Tyler et al. (1994) presented a temperature-dependent variation of α_{ox} = 0.00046/K, with increasing temperatures causing a decrease in α_{ox}, thus an increase in f_0. In a seasonal variation study, Chanton and Liptay (2000) obtained the following dependence relationship: α_{ox} = 0.000435/°C, where α_{ox} varied between 1.025 (at 35°C) and 1.049 (at 8°C), with the latter being among the greatest values found in the literature.

According to the study by Chanton and Liptay (2000), α_{ox} does not vary as a function of soil texture. Liptay et al. (1998) also reported that differences between clayey and sandy soils didn't affect the α_{ox} value, despite varying oxidation efficiencies. Tyler et al. (1994) observed that moisture content affected the α_{ox} value.

The isotopic fractionation factor associated with gas transport (α_{trans}) is assumed to be 1.0, which supposes that CH_4 transport across the PMOB is dominated by advection (Liptay et al. 1998; Abichou et al. 2006b; Stern et al. 2007), a process that does not cause isotopic fractionation (Liptay et al. 1998). Recent laboratory experiments by De Visscher et al. (2004) have shown that this approach can underestimate CH_4 oxidation by not taking into account diffusive flux, which can play a significant role in gas transport. If diffusive transport becomes important, then α_{trans} would be greater than 1. However, several authors (including De Visscher et al. 2004; and Stern et al. 2007) cite the works of Czepiel et al. (1996; 2003) who claim that the assumption of a preponderance of advective flux is supported by observations of a strong negative relationship between CH_4 emission and atmospheric pressure at several landfills. This is particularly true for landfill sites without gas collection systems.

3. Materials and Methods

Experimental plots

Three experimental plots measuring 2.75 m (W) × 9.75 m (L) were constructed with a slope of 3.5%, in the middle of an already capped area of the St-Nicéphore landfill. The final cover in this area was constructed with a

thick (almost 3 m in certain areas) layer of silt placed directly on the waste mass (as required by law). In this paper, only details pertaining to two PMOBs, namely PMOB-1 and PMOB-3B, are presented.

PMOB-1 included a 0.80 m thick layer of substrate underlain by a 0.10 m thick transitional layer consisting of 6.4-mm clean gravel and a 2.0- m thick gas distribution layer (GDL) consisting of 12.7-mm clean gravel. This plot was fed directly by biogas coming from the 3.5-year old buried waste mass (Fig. 1). As a result, it was not possible to control (or to obtain) the upward flux of biogas. The substrate layer consisted of a mixture of sand and compost, composed of 5 volumes of compost (before sieving) and 1 volume of coarse sand (D_{10} = 0.07 mm; D_{85} = 0.8 mm). More details on the compost and the mixture can be found in Jugnia et al. (2008). The substrate layer was placed in four 0.2-m layers and compacted with a vibrating plate to obtain layers with an average density of 8.4 kN m^{-3} and total porosity (n) equal to 0.63. The specific density of the solids (G_s) of the sand-compost mixture is equal to 22.5 kN m^{-3}.

PMOB-3B (Fig. 2) was constructed using a coarser substrate that resulted from mixing one volume of the same material used as substrate in PMOB-1 with one volume of 6.4-mm gravel. The 0.3-m thick substrate was compacted to a density of 14.0 kN m^{-3} and total porosity equal to 0.48. The GDL included 0.10 m of 6.4-mm clean gravel as a transitional layer and 0.80 m of 12.7-mm clean gravel layer. Contrary to PMOB-1, PMOB-3B was lined with a 1-mm thick HDPE geomembrane (GM), protected against tearing by a geotextile sheet. This completely isolated this experimental plot from the existing silty cover and the waste mass. PMOB-3B was fed with biogas from a well installed exclusively for this study. The amount of biogas fed into the system was controlled by means of a valve and the flow could be monitored by a mass flow meter connected to a data acquisition system. A drainage system was installed at the lowest point to evacuate infiltrating waters.

The walls around each of the two PMOBs were thermally shielded from the outside environment by 0.15-m thick polystyrene panels. The goal was to prevent lateral migration of moisture due to thermal gradients, which could lead to preferential flow paths. Temperature sensors (TMC20-HD, from Onset), connected to a data acquisition system (HOBO U12, from Onset) and gas probes (aluminum tubes with an inner diameter of 10 mm that were capped at the top end with a septum) were permanently installed at 4 separate downgradient points and at 4 different depths (6 depths in the case of gas probes) in each profile (Fig. 3), making up for a total of 48 gas probes and 32 temperature sensors for the two PMOBs. Tensiometers (Low Tension Irrometer, from Irrometer Company) and water content sensors (EC-5, from Decagon) were also installed and connected to data acquisition systems, allowing for the determination of the degree of saturation. The temperature and water content probes were

connected to data loggers. Meteorological data, including air temperature, precipitation, atmospheric pressure and wind speed were continuously recorded by a weather station installed near the experimental plots.

Gas analyses

For each gas probe in a profile, gas samples were taken on a weekly basis. The equivalent to the volume of the aluminum tubes was initially purged using the same syringe that one hour later was again introduced through the septum to collect the gas sample. The volumetric concentrations of CH_4, CO_2 and O_2 in the collected samples were obtained using a portable landfill gas analyser (Portable Gas Meter, Columbus Instruments, OH) equipped with infrared sensors able to detect CO_2 and CH_4. It also has an electrochemical sensor able to detect the volumetric concentration of O_2.

In mid summer of 2007, samples were also collected at a depth of 0.05 m using a specially designed gas probe that was manually inserted in the soil at every sampling date. Due to the small volume of biogas collected at this depth, gas samples were stored in a vacutainer serum tube and analysed within 24 hours in the laboratory using a gas chromatograph (Agilent 3000A Micro GC, equipped with a TCD detector and two columns, Molsieve for CH_4 and O_2 and Plot Q for CO_2).

In order to draw concentration profiles, the CO_2 and CH_4 concentrations at the surface were assumed to be nil due to dilution with atmospheric air (which does not mean that the CH_4 surface fluxes were exactly equal to zero). The O_2 volumetric concentration in the air, at the surface, was assumed to be equal to 20.9%. The N_2 concentrations were not obtained by direct measurement, but calculated as the difference between 100% and the sum of the concentrations of the three other gases (CO_2, O_2 and CH_4). As compared to O_2, N_2 is more relevant in indicating the aeration level, because it is neither consumed by oxidation near the surface nor by soil respiration. This was calculated for each depth within the several profiles analysed.

Stable isotope analyses

Samples for stable isotope analyses were taken at selected dates and locations in order to study oxidation efficiencies of four types of profiles, which are presented in the Results section. Samples were usually taken from the deepest gas sampling tube – that contains raw landfill gas – and from the top-most gas tube (0.10 m; in one case, 0.05 m). For 3 selected profiles, samples were also taken from approximately mid-depth (0.3 or 0.4 m) of the substrate layer.

For all the selected dates, a sample for stable isotope analysis was taken during surface flux measurements, which were performed on a weekly basis at several locations at each of the plots, following the static chamber method, as described by Fécil et al. (2003). In the present study, the sample was taken while the concentration within the chamber was still increasing.

Isotope analyses were performed at the Delta-Lab (Geological Survey of Canada, GSC-Quebec). The GC-C-IRMS system consists of a HP 5890 Series II Gas Chromatograph (GC) coupled with a VG Prism III Isotopic Ratio Mass Spectrometer (IRMS) via a combustion interface VG Isochrom II. The GC column was a PoraPlot Q (Varian, CP-7551) plot-fused silica column (25 m, 0.32 mm). The results obtained were normalized (re-calculated versus VPDB) using three internal gas standards. Two of them (BISO-1, HISO-1) were mixtures of 0.25% of methane and air. These were calibrated versus VPDB at the University of Victoria, BC. The third gas, CO_2 had a $\delta^{13}C$ value different from the reference gas. The latter was obtained from the BOC and calibrated versus VPDB at the Delta-Lab. The precision and accuracy for the standards were better than ± 0.4‰.

The fractionation factor for bacterial oxidation, α_{ox}, was calculated based on values found in the literature pertaining to landfill emission studies (Table 1). Only values in the range of temperatures found during the present study were considered. The average α_{ox} value, 1.0235, was the one adopted. Since α_{ox} is temperature dependent, a correction had to be applied (see Table 2) using Eq. (3), which is based on Tyler et al.'s (1994) temperature dependence relationship:

$$\alpha_{ox} = \alpha_{ox}\text{average} + 0.00046[20 - \text{T}(^{\circ}\text{C})] \text{ or } \alpha_{ox} = \alpha_{ox}\text{average} + 0.00046[293.15 - \text{T(K)}] \quad (3)$$

Eq. (3) shows that as temperatures rise above 20°C, lower values of α_{ox} are obtained, which, according to Eq. (2), leads to higher oxidation efficiencies, f_0.

4. RESULTS AND DISCUSSION

Gas concentration profiles

The gas concentration profiles corresponding to the dates when samples were selected for stable isotope analyses are presented in Fig. 4. Four types of typical profiles were identified and are described in the following.

Type 1 profiles (Fig. 4a, b) represent the periods during which the CH_4 concentration did not change much as biogas migrated up towards the atmosphere. This means that the system was not efficient in oxidizing the entire methane loading, at least up to the top-most gas sampling point, located 0.10 m below the surface. However, this does not mean that oxidation was not taking place. In fact, despite the poor CH_4 oxidation efficiency, a significant portion of the estimated CH_4 loading was oxidized (Table 2). Above the 0.10 m point it is possible that further oxidation may have taken place, but no monitoring was made to verify that.

Type 1 profiles can be associated with several factors affecting aeration of the substrate, including high degrees of water saturation, S_w, (and thus a decrease in air-filled porosity) and high upward biogas fluxes. The hypothesis of high S_w near the surface for Type 1 profiles do not hold, because S_w values were similar to those found in other situations where the oxidation efficiency was high (discussed below). The observed sharp decrease in N_2 near the surface (Fig. 4a,b) suggests poor aeration and points to high upward biogas loading as an important factor contributing to give the profile its shape. As far as evaluation of aeration is concerned, N_2 is a better indicator than O_2 because it is neither consumed by oxidation near the surface nor by soil respiration. Although we did not have any control on the magnitude of the CH_4 loading (the GDL sits directly on the waste mass), an estimate of the loading was made (see Table 2) based on loading data and the CH_4 oxidation efficiency of the system, f_0. The latter is given by stable isotope data, which is presented and commented below.

With Type 2 (Fig. 4 c, d) the CH_4 concentration didn't change up to a depth of approximately 0.4 m, and then decreased slightly, with the CH_4 concentration at the uppermost sampling point (0.1 m), remaining high. The observed deeper penetration of N_2 associated with Type 2 profiles is an indication that the upper part of the substrate was better aerated, which should favour oxidation. The surface flux obtained on Sept 24th was still high but much lower than in the case of Type 1, which was consistent with the deeper penetration of N_2. However, the quite high flux obtained in all surface measurements made at PMOB-1 on June 26th (Table 2) is bewildering. Two possible explanations can be offered: the first is that the locations of the profiles do not correspond exactly to the locations where surface flux measurements were conducted. In this case, the static chamber may have been placed exactly above a micro-fissure that was impossible to detect visually; as a consequence, a very high flux was measured. A second plausible cause for the high flux on June 26th is related to unequal moisture distribution within the substrate, a phenomena associated with unsaturated flow of water through the cover, which may lead to heterogeneous (or non uniform) gas distribution within the PMOBs (Cabral et al. 2007). This, combined with potential preferential flow, may also explain the high flux measured.

While oxidation may be taking place near the surface, dilution of the pore gas also contributes to the decrease in CH_4 concentration from 0.1 to the surface. In addition, part of the incoming O_2 is consumed by soil respiration.

Type 3 (Fig. 4e, f, g) corresponds to profiles where a steady decrease in CH_4 concentration was observed almost throughout the substrate (note that the substrate for PMOB-3B starts at the 0.3 m mark; Fig. 4g), although the concentrations of CH_4 at a depth of 0.1 m were still not negligible. One is tempted to associate these types of profiles with favourable conditions leading to a much deeper penetration of atmospheric air (see N_2 profiles in Fig. 4e, f, g), such as low degrees of saturation or increasing atmospheric pressure. The relatively high surface flux obtained on June 11th is also puzzling, given the quite effective penetration of atmospheric air. Finally, given the greater potential for dilution near the surface and the surprisingly low O_2 concentration below 0.1 to 0.2 m (in part due to respiration), stable isotope data become an important tool to evaluate the actual oxidation efficiency of systems identified by these types of profiles.

The last one, Type 4 (Fig. 4h), represents profiles observed in PMOB-1 for nearly two consecutive weeks of dry weather, during the summer of 2007. Evidence of dryer substrate is found in the value of S_w at the bottom of the substrate, which is the lowest of all shown in Fig. 5 for PMOB-1 (S_w = 82.1%). In addition, the surface flow was below detectable limits and the nearly vertical N_2 concentration profile (Fig. 4h) clearly indicates that the substrate was well aerated throughout its depth. The CH_4 concentration, which was already relatively low (28.8%) at 0.82 m, decreased to quite low levels (~1%) at 0.3 to 0.4 m. The relatively high O_2 concentration at 0.6 m may have resulted from a measurement error; otherwise, the Authors cannot find any other plausible interpretation for this odd datum. The quite low concentrations of CH_4 near the surface cannot be associated with oxidation alone. As mentioned previously, soil respiration and dilution of the pore gas also have to be considered and stable isotope results become a useful tool to evaluate the extent of oxidation. Although it is impossible to verify (using either our data or site records), the CH_4 loading might have been quite low during the two-week period during which the Type 4 profile was obtained, allowing for the large extent of diffusive ingress of atmospheric air.

According to Chanton and Liptay (2000), and Stern et al. (2007), the optimum soil temperature for CH_4 oxidation appears to be from 25 ºC to 30 ºC. With the exception of the profile obtained in PMOB-3B (Fig. 5g), where temperatures remained in the vicinity of 30 ºC, for all the other dates for which sampling for isotope analyses was performed, the temperatures remained in the vicinity of 20 ºC. The lowest air temperature during the monitoring period was approximately 15 ºC and the highest reached approximately 30 ºC. For all sampling times, the air temperature (shown in Fig. 5 as the value at the surface) was always slightly lower than the temperature at 0.1 m.

$\delta^{13}C$ Values and oxidation efficiencies

Table 2 presents the results of stable isotope analyses for the 4 types of profiles. The $\delta^{13}C$ value of methane from the waste mass (δ_A), or baseline CH_4 concentration value, was obtained by applying Eq. (1) to stable isotope data obtained at 0.82 m depth, even in the case of PMOB-3B.

When the CH_4 oxidation efficiency was calculated from the baseline (0.82 m) to the surface, δ_E corresponded to the $\delta^{13}C$ value obtained from samples collected during static chamber tests (thus at the surface). When the oxidation efficiency was calculated from 0.82 m to the top-most gas probe (0.10 m from the surface), δ_E corresponded to the $\delta^{13}C$ value obtained at 0.10 m. The same applied to the oxidation efficiencies related to 0.05; 0.30 and 0.40 m depths; δ_E corresponded to the $\delta^{13}C$ value obtained at these depths, respectively.

The interpretation of the results of stable isotopes is made in two phases: the first deals with f_0 calculated using the $\delta^{13}C$ obtained at the 0.05, 0.1, 0.3 and 0.4 m depths; the second will discuss the f_0 values obtained from samples collected during static chamber tests, i.e. at the surface.

Oxidation efficiency based on stable isotope probing of soil gas profiles

Type 1 and Type 2 profiles exhibited low values of f_0, because of the estimated high biogas loadings and poor aeration of the substrate. In the case of Type 3 profiles, the oxidation efficiencies were much higher and reached 88.7% at 0.1 in PMOB-3B (the oxidation efficiency obtained at 0.05 m is discussed later in the text). It appears that oxidation was already detectable at the base of the 0.3-m thick substrate, where f_0 = 18.4%. In addition, the CH_4 concentration at 0.82 m (depth at which δ_A was taken) was lower than usual baseline values of raw landfill biogas. It can be deduced that, if f_0 were to be calculated using the average δ_A in the present study (-57.9‰), the f_0 value would have been 100%; in other words, the system in PMOB-3B for Sept 24, 2007, would have been 100% efficient.

Methane oxidation efficiency calculations for PMOB-3B can also be made based on mass balance calculations, and then compared to stable isotope analyses (e.g. Powelson et al. 2007). In the present study, mass balance calculations were made using loading and surface flux measurements for PMOB-3B only (loading data were not available for PMOB-1 since it sits directly on the waste mass). For the sole result from PMOB-3B (Sept. 24th), the surface flux was 4.3 l m^{-2} h^{-1} (Table 2), whereas the CH_4 loading was in the vicinity of 15 l m^{-2} h^{-1}, which results in a CH_4 oxidation efficiency of 70%. The f_0 obtained using stable isotope was equal to 55.6% (data is taken from surface (chamber test) measurements. Several factors can explain this discrepancy, including: 1) the sensitivity of f_0 to slight changes in the isotopic fractionation factor for bacterial oxidation, α_{ox}; [for example, adoption of (α_{ox} - σ) =

1.0188 (see Table 3, whose results are discussed later in the text), instead of the average value considered; i.e. α_{ox} = 1.0235) would have led to f_0 = 68.9% (Table 3), i.e. practically the same oxidation efficiency obtained by mass balance]; 2) uncertainties related to the static chamber method; and 3) uncertainties related to mass flow meter readings (the values read were close to the margin of error of the equipment). Powelson et al. (2007) attributes the discrepancy in part to oxidation of a portion of the inflow gas. Irrespective of this discrepancy, the results of the stable isotope analysis did help confirm that oxidation was occurring and that the system was very efficient in reducing CH_4 emissions.

Despite deeper penetration of atmospheric air within the substrate of PMOB-1 than within PMOB-3B for Type 3 profiles, as evidenced by the more abrupt N_2 profiles within the substrate of PMOB-1 (Fig. 4f, g and h), the values of f_0 obtained at 0.1 m for PMOB-1 (45.1% and 64.4%, for June 11th and Aug. 20th, respectively; Table 2) are lower than that obtained for PMOB-3B (88.7% at 0.1 m). In addition, the CH_4 surface flux on Aug. 20th at PMOB-1, profile 1 is four times lower than the flux measured on Sept. 24th on the surface of PMOB-3B (Table 2). The higher temperatures existing in PMOB-3B on Sept 24th (Fig. 5g) might be partly responsible for this. According to the Q_{10}-rule, reaction rates increase by approximately a factor of 2 for every 10 °C increase in temperature. This given, temperatures in the vicinity of 30 ºC in PMOB-3B may have induced higher CH_4 oxidation rates than the temperatures in the vicinity of 20 ºC found in PMOB-1. Moreover, as previously discussed, temperature also has an important effect on the value of α_{ox}, thus on f_0 (e.g. Coleman et al. 1981; Chanton and Liptay 2000). This also justifies why the values of α_{ox} in Table 2 (fourth column from the right) that were used in the calculation of f_0 were adjusted to consider the temperatures prevailing during sampling. In PMOB-3B there was a depletion (decrease in $\delta^{13}C$) between 0.1 and 0.05 m, which may be associated, at least in part, with one of the three phenomena that led to loss of enrichment in CH_4-$\delta^{13}C$ values measured at the surface (see discussion in the next subsection).

As far as the Type 4 profile is concerned, on July 17th the CH_4 concentrations at depths reaching 0.4 m were already rather low and the oxidation efficiency in PMOB-1 reached 89.7% at 0.1 m (Table 2). A significant portion of the oxidation occurred within the bottom-most 0.4 m of substrate, with f_0 = 69.1% at 0.4 m. It can be observed that the temperatures within the substrate (Fig. 5h) were not as high as those measured within PMOB-3B (Fig. 5g), indicating that other factors contributed to the high f_0. Indeed, excellent aeration of the substrate, as evidenced by the nearly vertical N_2 profile (Fig. 4h) helps to explain the high oxidation efficiency obtained.

Following the same line of thought used for the interpretation of the data from PMOB-3B, if a typical δ_A were used (-57.9‰, rather than -56.0‰), the CH_4 oxidation efficiency of PMOB-1, calculated using Eq. (2), would be

99% at a depth of 0.1 m, i.e. the system could be considered 100% efficient for the two-weeks represented by the profile obtained on July 17, 2007.

On July 17th, the CH_4 concentration at 0.82 m depth (28.8%) was much lower than the typical value observed on the investigated landfill biogas (~ 58%). This indicates that some oxidation was possibly occurring within the gas distribution layer. Gebert and Gröngröft (2006) also showed high CH_4 oxidation rates obtained with coarse, purely mineral material in a biofiltre experiment. In the present case, dilution played an important role. Indeed N_2 penetrated very deep down and its concentration at the interface with the GDL was as high as 36.7%. According to the data presented in Table 2, the $\delta^{13}C$ value (- 56.0‰) was in the lower range of values recorded for raw biogas in this study. If a typical $\delta^{13}C$ value of the anoxic zone (δ_A) were used, the oxidation efficiency at the base of the substrate would be in the vicinity of 10%, showing that some oxidation might be occurring within the GDL. However, this oxidation is limited by the lack of O_2, which was mostly depleted near the surface. In conclusion, the low CH_4 concentration at the base of the cell is mainly a result of dilution with atmospheric components.

Oxidation efficiency based on stable isotope probing of static chambers

The data in Table 2 show that there is a clear loss of enrichment in CH_4-$\delta^{13}C$ values between 0.1 m and the surface, i.e. the values become more negative, except for PMOB1-P4, on Sept. 24th, when it remained almost unaltered. In the case of the representative Type 4 profile, there is an almost entire loss of enrichment. According to Chanton et al. (2008), there are three possible mechanisms causing the loss of enrichment: diffusive fractionation, bypass mixing, and differential flow path oxidation. The first relates to the faster migration of $^{12}CH_4$ (De Visscher et al. 2004), which causes an enrichment CH_4-$\delta^{13}C$ in the sub-surface ($^{13}CH_4$ is left behind), thus a consequent loss of enrichment at the surface (greater $^{12}CH_4$ concentration). The second reason, bypass mixing, results from a mix of oxidized and non-oxidized biogas at the surface. The non-oxidized biogas would reach the surface through macropores or fissures, thereby bypassing, at least in part, contact with methanotrophs. If the gas probes do not intercept the macropores or fissure, a higher (or less negative) $\delta^{13}C$ is obtained. Finally, according to Chanton et al. (2008), differential flow path oxidation is related to situations where there is complete oxidation of CH_4 in a particular flow path, whereas in another flow path CH_4 is not or is much less oxidized. The first, a “dead end” flow, does not contribute to the same extent to the overall oxidation efficiency. Chanton et al. (2008) hypothesize that the surface values would constitute a low limit for CH_4 oxidation efficiency estimation, whereas the values obtained from gas probes would constitute un upper limit.

The above mentioned hypotheses were neither verified, nor investigated in detail within the scope of the present study. One idea to investigate what is actually happening would be to improve the methodology to sample very near the surface (less than 0.05 m). Given the heterogeneities within normal final covers, and the possibility of preferential flow (such as alluded to by Chanton et al. (2008)), one might consider taking several shallow samples over an extended area, in a very short period of time (preferably as simultaneously as possible), in order to obtain a representative set of values. Again, this procedure was not tested within the scope of the present paper, but will be considered for future work.

Considerations about the influence of the adopted α_{ox} on f_0

Since α_{oxs} was calculated based on values from previous studies (Table 1), we performed a sensitivity analysis of f_0 to variations in α_{ox} ± standard deviation (σ) of the data presented in Table 1. The results presented in Table 3 show that with $\alpha_{ox} + \sigma$), which represents a meagre 0.5% variation in α_{ox}, the values of f_0 decrease by an average of 16%. When $\alpha_{ox} - \sigma$ is adopted, f_0 increases by an average of 24%. The increase or decrease in efficiency leads to an equivalent change in the magnitude of both the estimated CH_4 loading and the estimated rate of CH_4 removal (values not show in Table 3). In the case of samples from Sept. 24th (PMOB-3B) and July 17th (PMOB-1), the adoption of $\alpha_{ox} - \sigma$ resulted in oxidation efficiencies greater than 100%, which is impossible (maybe $\alpha_{ox} - \sigma$ is too low a value for the isotopic fractionation factor). Overall, it appears from this analysis that slight variations in the adopted isotopic fractionation factor have a measurable influence on the CH_4 oxidation efficiency of the cover system.

Considerations concerning the adopted fractionation factor, α_{trans}

As discussed previously, the consideration of α_{trans} equal to 1.0 is reasonable insofar as gas transport is dominated by advection. In the case of PMOB-3B, the biogas loading was high (~ 15 l m^{-2} h^{-1}) with the diffusive flux representing less than 2% of this loading. The diffusive flux was determined using Fick's first law, the average concentration gradient between the bottom and the top of the PMOB and the diffusion coefficient of the material (data not presented). Therefore, the assumption $\alpha_{trans} = 1$ seems plausible (see also Background section). With respect to PMOB-1, loadings could not be controlled because the GDL sits directly over the waste mass. It is thus necessary to rely on surface flux measurements, which, as shown in Table 2, are also high, with the exception of the fluxes obtained on Aug. 20th and July 17th.

For the latter two dates, a closer look into this issue would be necessary. For example, Rannaud et al. (2008) showed that a pressure differential (Δp_bar) equal to 0.05 kPa (equivalent to a 5 mm column of water) was required to reproduce a CH_4 concentration profile obtained in the field during the summer of 2006, using the TOUGH2-LGM simulator (Nastev 1998). This profile showed a marked reduction in CH_4 concentrations near the surface, as is the case for the profiles obtained on Aug. 20th and July 17th. With such a low, yet realistic pressure differential (the values of Δp_bar a few hours before sampling were in the vicinity of 0.05 kPa; data not presented), and considering the values of the degree of water saturation existing in PMOB-1 on the same dates ($S_w \approx 70\%$), Rannaud et al. (2008) obtained the diffusive and advective fluxes using TOUGH2-LGM. The diffusive flux (~ 0.14 l m^{-2} h^{-1}) was nearly one order of magnitude higher than the advective flux. Under such conditions, the assumption of $\alpha_{trans} = 1$ would have led to an underestimation of the oxidation efficiency should stable isotopes be used to calculate it (De Visscher et al. 2004). No further investigation into this issue was performed.

5. Summary and concluding remarks

Stable isotope analyses were performed in order to evaluate the biotic methane oxidation efficiencies of two experimental biocovers installed at the St-Nicéphore landfill, Quebec, Canada. Methane concentration profiles in the substrate were divided into four types, varying from profiles showing almost no to limited decrease in the vertical CH_4 concentration (Types 1 and 2) to profiles where there is a clear decrease in CH_4 concentration near the surface (Type 3), or even deep inside it (Type 4).

The sharp decrease in CH_4 concentration observed near the surface in all cases, and deeper down in other cases, cannot guarantee that oxidation was the only phenomenon taking place. Indeed, part of the decrease was due to atmospheric air penetration, thus dilution of the pore gas. Stable isotope analyses became a useful tool to calculate oxidation efficiency in a system where soil respiration competes for the same incoming O_2.

The results of stable isotope analyses showed that the substrates of the two PMOBs were indeed able to promote CH_4 oxidation. This was evidenced by the enrichment in the ^{13}C isotope in the upward migrating biogas, due to preferential use of the ^{12}C isotope by methanotrophic bacteria. Oxidation efficiencies calculated for a depth of 0.1 m from the surface varied from 2.9 to 89.7% in PMOB-1, and was equal to 88.7% for a representative profile of a relatively dry period in PMOB-3B. In some cases, the amount of CH_4 oxidized was high, but the loading was also too high, resulting in poor oxidation efficiency, in spite of the higher absolute rate of methane removal.

The analysis of the results shows that one single factor cannot explain the high or low oxidation efficiencies obtained. Indeed, a set of factors governed the response of the system. For example, despite the relatively low degree of saturation prevailing near the surface in most of the situations investigated, poor aeration of the substrate was observed in certain cases, leading to quite low efficiencies (profiles of the Types 1 and 2). It is impossible to affirm that poor aeration was partly caused by high upward biogas fluxes, since loading could not be controlled in PMOB-1. However, the assumption of high loadings seems to hold for Type 1 and Type 2 profiles, given the fact that CH_4 oxidation remained very low and surface fluxes were the highest.

Another factor that could partly explain high or low efficiencies is the temperature within the substrate. In the present study, despite the fact that it was more than 10 ºC lower within the profile of PMOB-1 on July 17th (Fig. 5h) than within the profile of PMOB-3B on Sept. 24th (Fig. 5g), the oxidation efficiencies calculated at 0.1 m were quite high for both (89.7% and 88.7%, respectively). In this case, the higher surface flow in PMOB-3B seems to be limiting O_2 penetration, while the non-detected flow near the surface of PMOB-1 and deep penetration of N_2 indicated that oxidation was being favoured within PMOB-1 on July 17th (Fig. 4g).

A loss of enrichment in CH_4-$\delta^{13}C$ values was observed between the upper-most probe (located 0.1 m below the surface) and the surface. Chanton et al. (2008) refer to four mechanisms that could be at the origin of such behaviour. However, the actual causes for the loss of enrichment were not investigated in detail within the scope of the present study. It is suggested to improve the methodology of sampling very near the surface and develop a field program whereby several shallow samples would be collected over an extended area and in a very short period of time. With this extended dataset, one might be able to identify more clearly the reasons for the loss of oxidation efficiency near the surface.

Due to a number of reasons, the oxidation efficiencies obtained in this study have to be considered as indicators of the real efficiencies. One of these reasons is that the actual fractionation factor values were not determined specifically for the study. A sensitivity analyses of f_0 to variations in α_{ox} showed that slight variations in the adopted α_{ox} has a measurable influence on the oxidation efficiency of the system. Subsequently, efficiency analyses based on stable isotope probing have to be interpreted with adequate caution. Another reason for considering the values of f_0 as indicators is that α_{ox} is directly influenced by soil temperature; the latter being a parameter that continuously changes. For a more precise evaluation of oxidation efficiencies, a study considering both short and long term variations of f_0 would be recommended.

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α_{ox}	Soil temperature	Reference
1.0140	25°C	Liptay et al., (1998)
1.0220		
1.0300		
1.0235	22°C	Chanton et al., (1999)
1.0288	9°C	
1.0307	5°C	
1.0311	4°C	
1.0315	3°C	
1.0304	6°C	
1.0240	20°C	
1.0266	15°C	
1.0269	13°C	
1.0240	21°C	
1.0241	20°C	
1.0316	3°C	
1.0244	-	Chanton et al., (2008)
1.0250	35ºC	Chanton e Liptay (2000)
1.0490	8ºC	

Table 1 - Values of *αox* found in the literature with associated soil temperature

Type of profile	Selected dates (2007)	PMOB (Profile)	Surface flux CH_4 (l m^{-2} h^{-1})	Depth (m)	Vol. CH_4 concentr. (%)	$\delta^{13}C$ of CH_4 (δ_A at 0.82 m) (‰ VPDB)	α_{ox} (corrected for temper.)[1]	fo (%)	Estimated CH_4 loading (l m^{-2} h^{-1})	Estim rate of CH_4 removal (l m^{-2} h^{-1})
1	July 4th	PMOB-1 (P1)	78.2	Surface	4.8	-56.7	1.0245	2.9	80.5	2.3
				0.1	49.8	-57.7	1.0220	0.0	78.2	0.0
				0.82	56.0	-57.4	-	-	-	-
	Sept. 24th	PMOB-1 (P4)	107.4	Surface	4.7	-54.6	1.0240	15.0	126.4	19.0
				0.1	44.9	-55.6	1.0209	12.2	122.3	14.9
				0.3	48.8	-57.6	1.0220	2.7	110.3	2.9
				0.82	58.8	-58.2	-	-	-	-
2	June 26th	PMOB-1 (P4)	458.2	Surface	15.7	-56.8	1.0219	3.7	475.6	17.4
				0.1	35.1	-54.6	1.0194	15.4	541.9	83.7
				0.82	58.2	-57.6	-	-	-	
	Sept. 24th	PMOB-1 (P1)	24.4	Surface	0.3	-55.5	1.0240	10.5	27.3	2.9
				0.1	36.5	-52.7	1.0208	25.2	32.6	8.2
				0.3	41.2	-52.2	1.0208	27.8	33.8	9.4
				0.82	53.6	-58.0	-	-	-	-
3	June 11th	PMOB-1 (P2)	21.4	Surface	-	-53.9	1.0248	22.6	27.7	6.3
				0.1	7.7	-49.7	1.0217	45.1	39.0	17.6
				0.82	58.3	-59.5	-	-	-	
	Aug. 20th	PMOB-1 (P1)	1.0	Surface	3.3	-53.6	1.0263	13.4	1.2	0.2
				0.1	5.0	-42.3	1.0231	64.4	2.8	1.8
				0.82	51.6	-57.2	-	-	-	-
	Sept. 24th	PMOB-3B (P3)	4.3	Surface	2.9	-42.4	1.0243	55.6	9.7	5.4
				0.05	0.3	-44.0	1.0212	56.4	9.9	5.6
				0.1	5.1	-41.7	1.0161	88.7	38.0	33.7
				0.3	41.9	-52.8	1.0170	18.4	5.3	1.0
				0.82	49.8	-56.0	-	-	-	-
4	July 17th	PMOB1 (P1)	Below detectable limits	Surface	0.0	-59.6	1.0240	0.0		
				0.1	1.2	-35.8	1.0225	89.7	Cannot be estimated	Cannot be estimated
				0.4	3.8	-39.9	1.0232	69.1		
				0.82	28.8	-56.0	-	-		

[1] The average α_{ox} value adopted (based on values found in the literature pertaining to landfill emissions studies; see Table 1) is 1.0235.

Table 2 - Results from stable isotope analyses and oxidation efficiencies (f_0).

Selected dates (2007)	PMOB (Profile)	Depth (m)	Surface flux CH_4 (l m^{-2} h^{-1})	f_o (%)	f_o (%) (with $\alpha_{ox} + \sigma$)[1]	% difference in relation to f_o calculated with α_{ox}	f_o (%) (with $\alpha_{ox} - \sigma$)	% difference in relation to f_o calculated with α_{ox}
July 4th	PMOB-1 (P1)	Surface	78.2	2.9	2.4	16.1%	**3.5**	**-23.7%**
		0.1		0.0	0.0	0.0%	**0.0**	**0.0%**
		0.82		-				
Sept. 24th	PMOB-1 (P4)	Surface	107.4	15.0	12.6	16.3%	**18.7**	**-24.2%**
		0.1		12.2	10.0	18.3%	**15.7**	**-28.9%**
		0.3		2.7	2.2	17.5%	**3.4**	**-27.0%**
		0.82		-	-		-	
June 26th	PMOB-1 (P4)	Surface	458.2	3.7	3.0	17.6%	**4.6**	**-27.2%**
		0.1		15.4	12.4	19.4%	**20.4**	**-31.8%**
		0.82		-	-		-	
Sept. 24th	PMOB-1 (P1)	Surface	24.4	10.5	8.8	16.3%	**13.0**	**-24.2%**
		0.1		25.2	20.6	18.3%	**32.5**	**-29.0%**
		0.3		27.8	22.7	18.3%	**35.8**	**-29.0%**
		0.82		-	-		-	
June 11th	PMOB-1 (P2)	Surface	21.4	22.6	19.0	15.9%	**27.9**	**-23.3%**
		0.1		45.1	37.1	17.7%	**57.5**	**-27.5%**
		0.82		-	-		-	
Aug. 20th	PMOB-1 (P1)	Surface	1.0	13.4	11.3	15.1%	**16.3**	**-21.7%**
		0.1		64.4	53.6	16.9%	**80.8**	**-25.4%**
		0.82		-	-		-	
Sept. 24th	PMOB-3B (P3)	Surface	4.3	55.6	46.6	16.2%	**68.9**	**-23.9%**
		0.05		56.4	46.2	18.1%	**72.4**	**-28.4%**
		0.1		88.7	68.7	22.6%	**125.2 (100%)**	**-12.8% (w/ 100%)**
		0.3		18.4	14.4	21.6%	**25.4**	**-38.1%**
		0.82		-	-		-	
July 17th	PMOB1 (P1)	Surface	Below detectable limits	0.0	0.0	0.0%	**0.0**	**0.0%**
		0.1		89.7	74.3	17.3%	**113.4 (100%)**	**-11.4% (w/ 100%)**
		0.4		69.1	57.5	16.8%	**86.5**	**-25.2%**
		0.82		-	-		-	

[1] Average α_{ox} = 1.0235; (α_{ox} + σ) = 1.0282; (α_{ox} - σ) = 1.0188; where σ is the standard deviation (all data from Table 1)

Table 3 – Results of sensitivity analysis of f_0 to changes in α_{ox}.

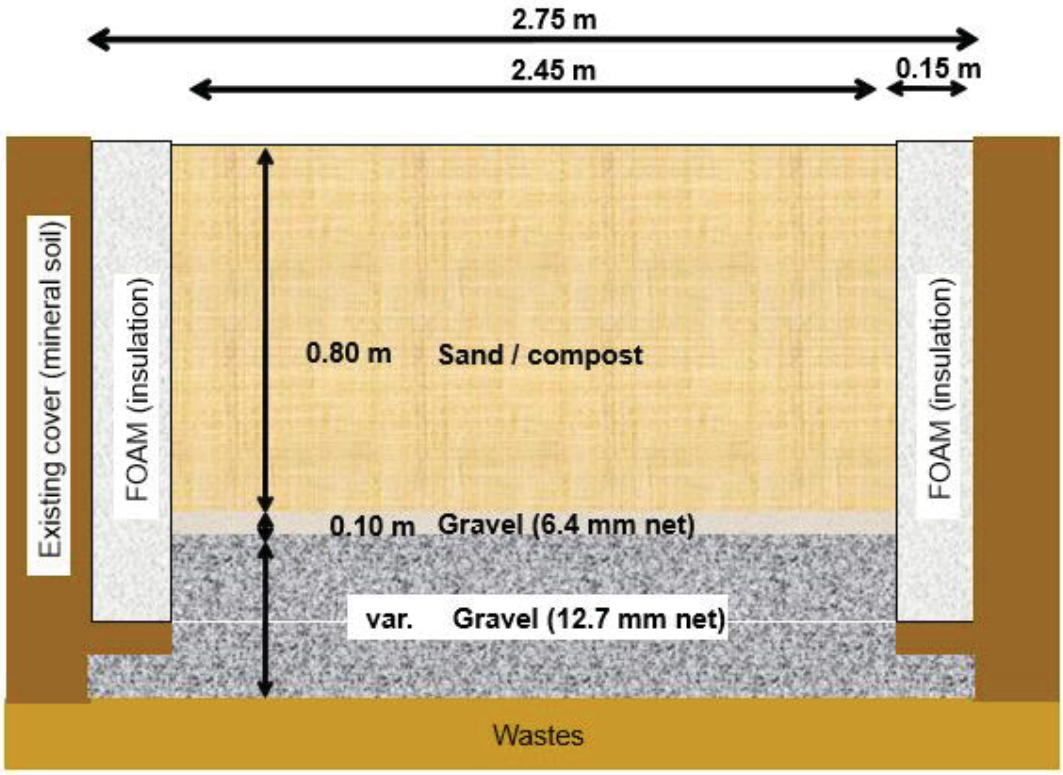

Fig. 1- Schematic representation of the setup of PMOB-1

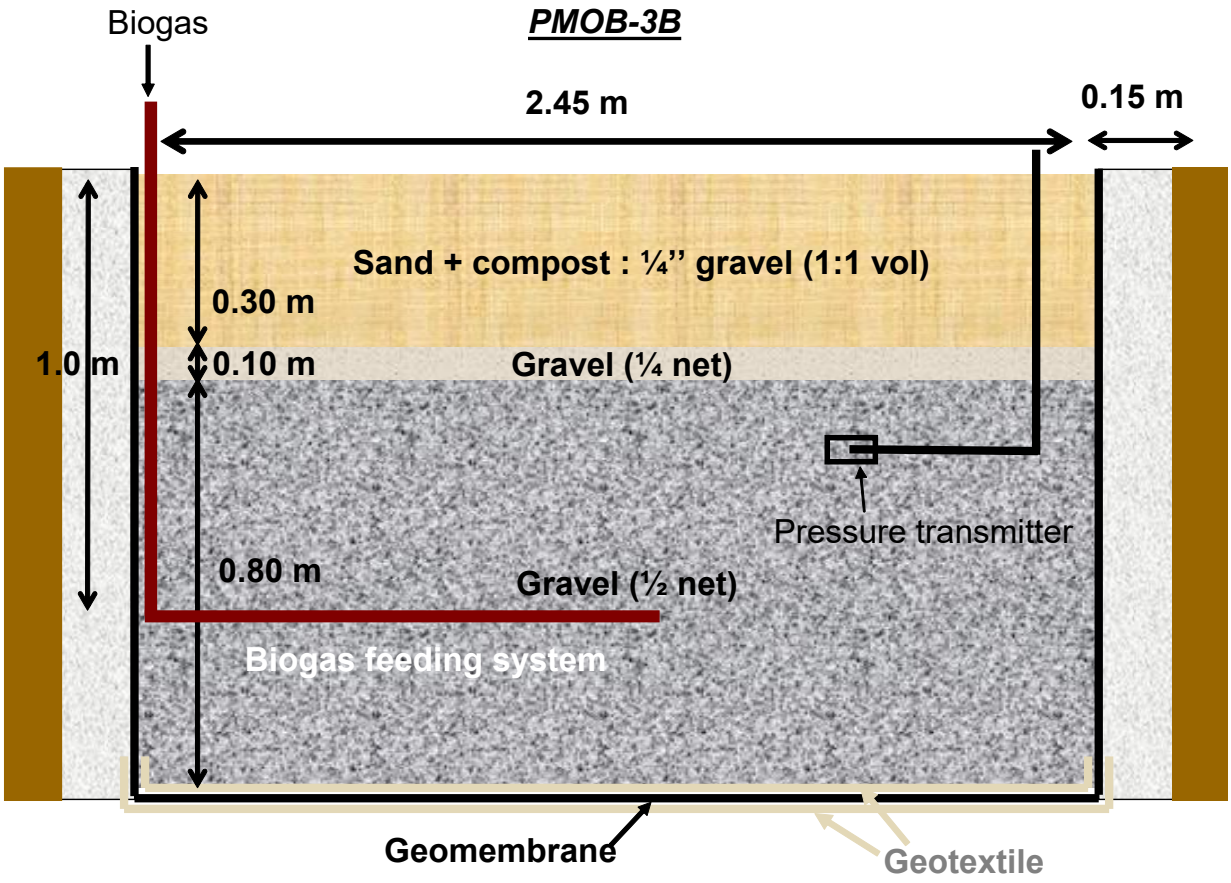

Fig. 2- Schematic representation of the setp of PMOB-3B

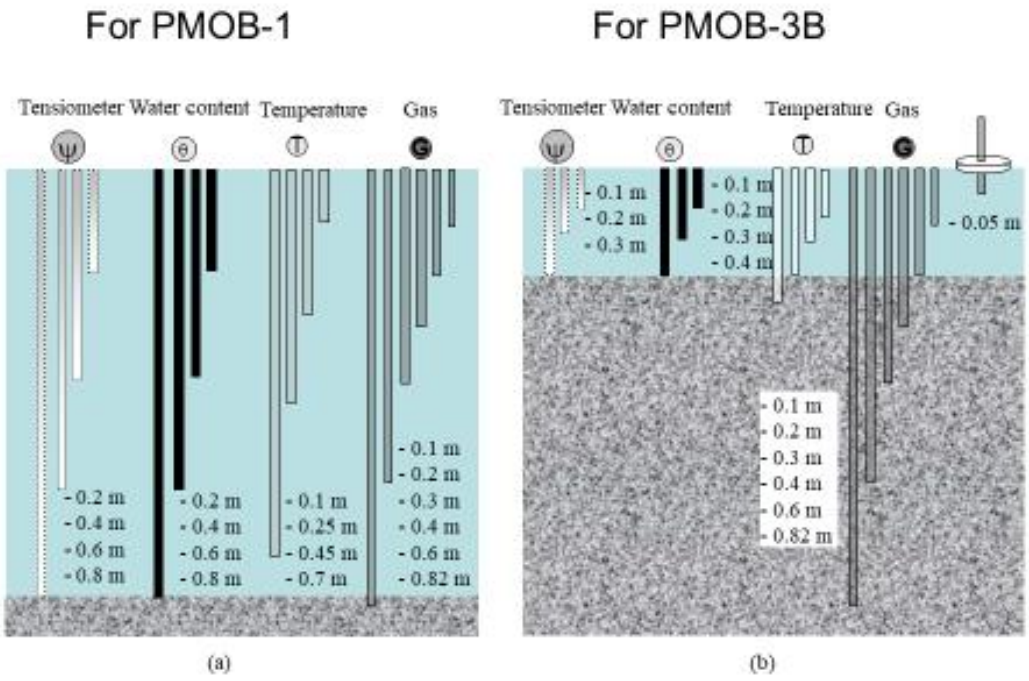

Fig. 3 - Instrumentation of the PMOBs

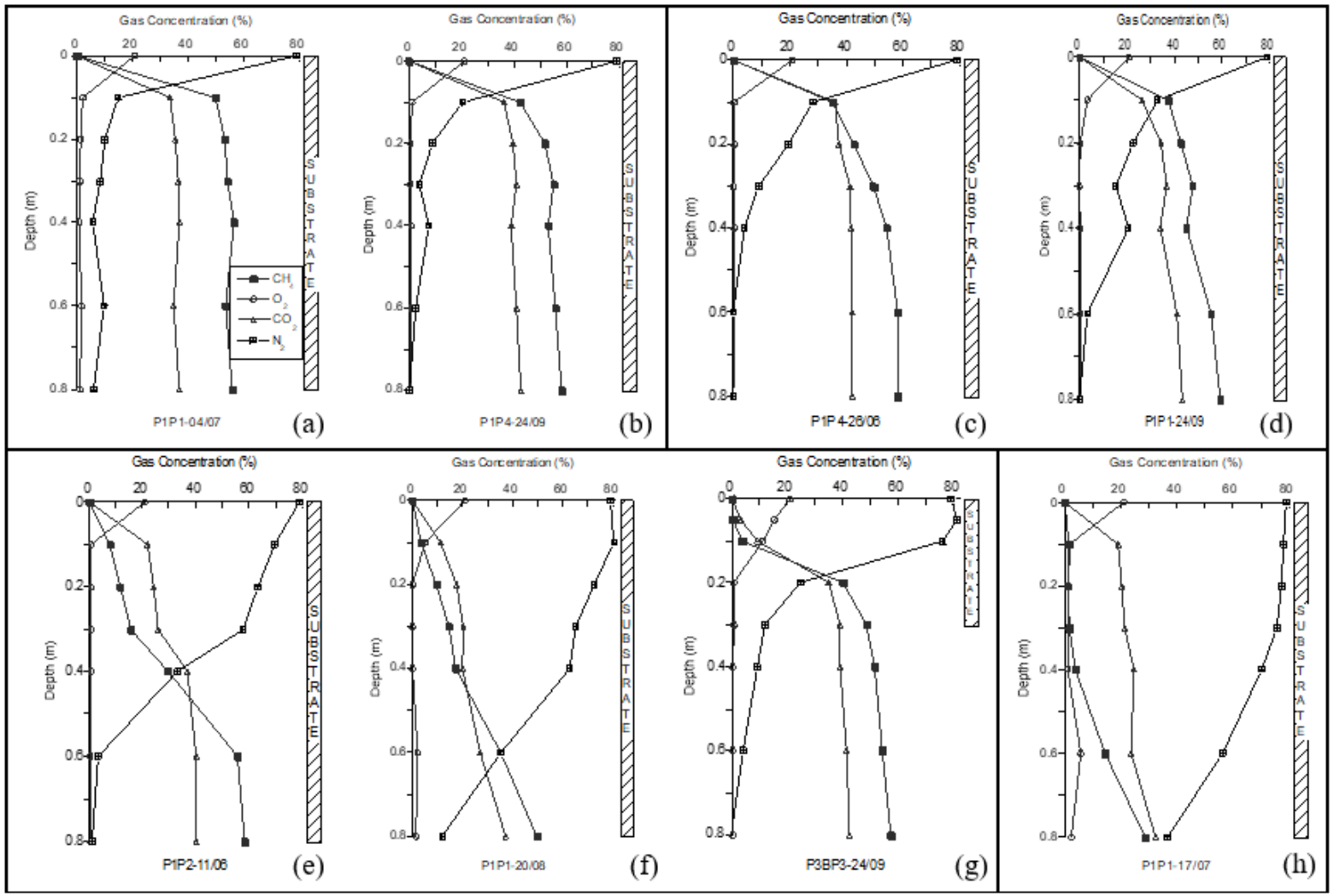

Fig. 4 - Selected gas concentration profiles for which samples were taken for stable isotope analyses: (a) and (b) are of Type 1; (c) and (d) of Type 2, (e) to (g) of Type 3 and (h) of Type 4

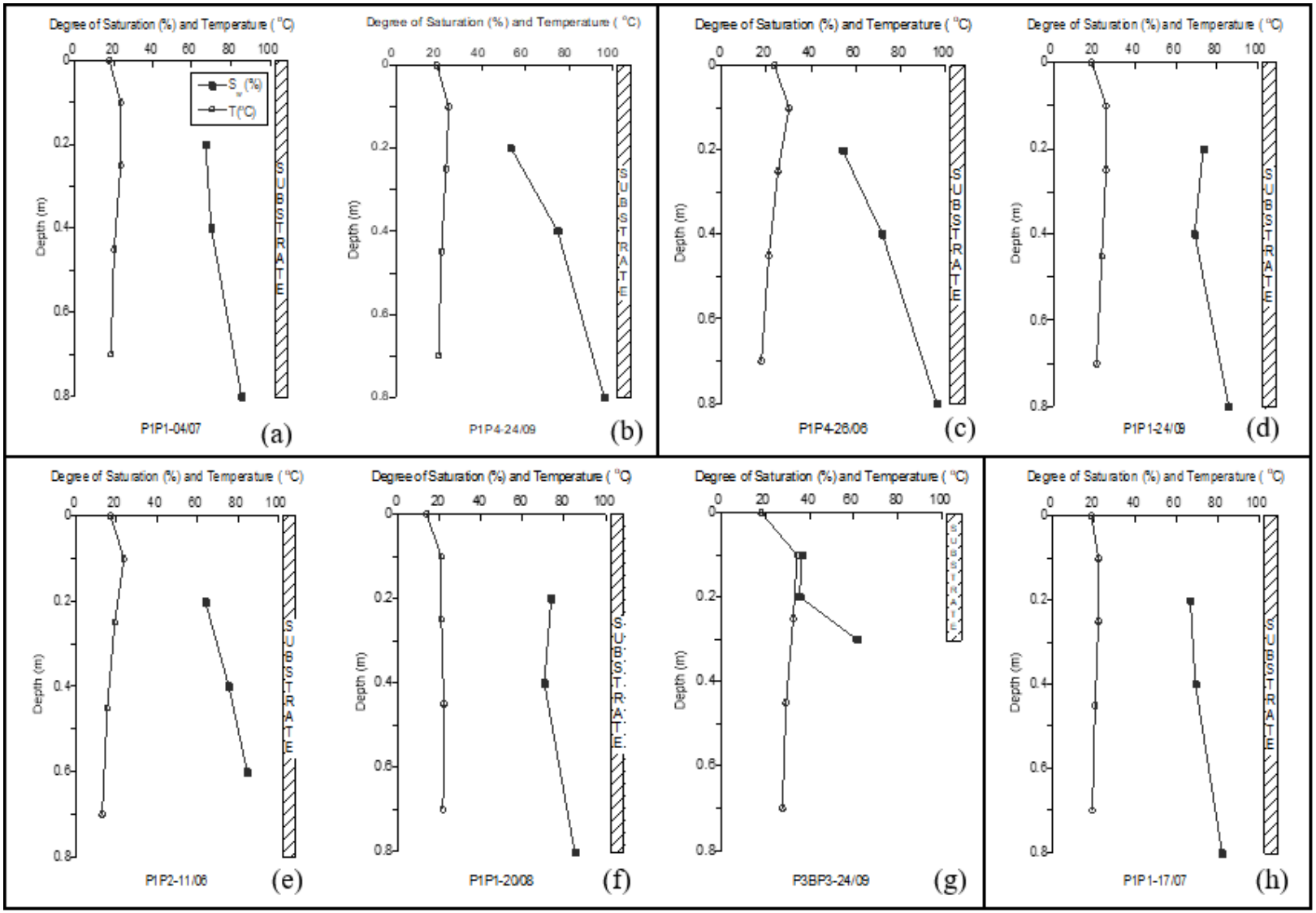

Fig. 5- Profiles of degree of saturation and temperature for the sampling dates